

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 933 824 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.08.1999 Bulletin 1999/31

(51) Int. Cl.⁶: H01M 2/16, H01M 10/40

(21) Application number: 99101376.4

(22) Date of filing: 26.01.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Spotnitz, Robert M.
San Remo, CA 94538 (US)
• Wensley, Glen C.
Rock Hill S.C. 29732 (US)

(30) Priority: 30.01.1998 US 16024

(71) Applicant: CELGARD LLC
Charlotte, NC 28273 (US)

(74) Representative:
von Kreisler, Alek, Dipl.-Chem. et al
Patentanwälte,
von Kreisler-Selting-Werner,
Bahnhofsvorplatz 1 (Deichmannhaus)
50667 Köln (DE)

(54) Separator for gel electrolyte battery

(57) A battery separator for a gel electrolyte battery includes a microporous membrane; and an adherent coating thereon, or a gel-forming coating thereon, the gel-forming coating including a gel-forming polymer and a plasticizer.

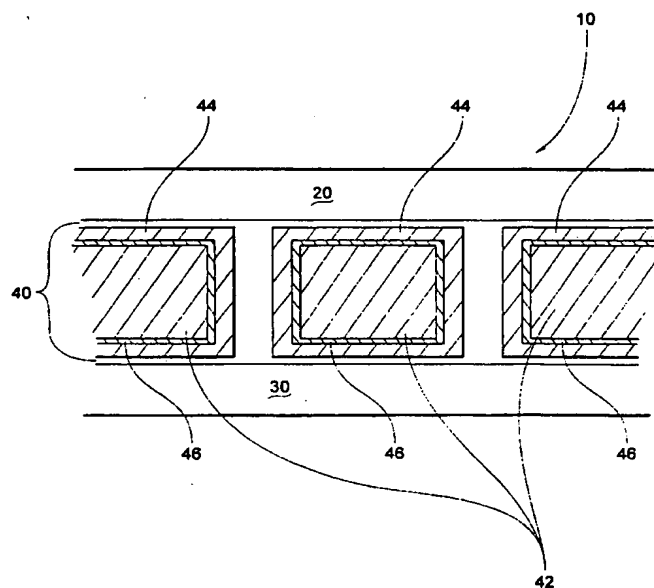


Fig. 1

EP 0 933 824 A2

Description

Field of the Invention

[0001] The instant invention is directed to a separator 5 for a gel electrolyte battery.

Background of the Invention

[0002] Lightweight rechargeable batteries are used in 10 many electrically powered devices, for example, cellular phones, pagers, computers, and power tools. One popular rechargeable battery is the lithium ion battery. Lithium ion batteries that are commercially available today use a liquid electrolyte. This electrolyte is organically based. Consequently, lithium ion batteries must be sealed in rigid 'cans' to prevent the leakage of the electrolyte. There is a desire to eliminate the rigid can and move toward flexible, light-weight, leak-tight packaging, e.g., metallised plastic or foil bags.

[0003] One method suggested for eliminating the can is the use of solid electrolytes. See U.S. Patent Nos. 5,296,318; 5,437,692; 5,460,904; 5,639,573; 5,681,357; and 5,688,293. Solid electrolytes include 15 two types, a solid electrolyte and a gel electrolyte. Of these two types, the gel electrolyte is preferred because of its greater conductivity. Gel electrolytes, however, are deficient because they cannot easily provide the structural integrity necessary to separate the positive and negative electrodes, for example, during manufacture, and to provide the shutdown capability necessary to safely handle the electrodes, for example, during an overcharge condition.

[0004] In U.S. Patent Nos. 5,639,573; 5,681,357; and 5,688,293, it is proposed that a microporous membrane (or inert layer), in combination with an absorbing or gel-forming polymer, be used as a separator system. After the electrolyte is injected into the separator system, the gel-forming polymer is cured to form the gelled electrolyte around the microporous membrane whereby the structural integrity of the gel electrolyte is enhanced by the inclusion of a microporous membrane.

[0005] In the manufacture of the foregoing battery, the occurrence of delamination or separation of the absorbing or gel-forming layer from the inert layer is detrimental. Accordingly, there is a need for a new separator which improves the adherence of the microporous membrane to the gel-forming polymer and thereby reduces delamination or separation of these two components during manufacturing.

Summary of the Invention

[0006] The present invention is to a battery separator, particularly useful in a gel electrolyte battery, including a microporous polymer membrane; and an adherent coating having a surface density $< 0.3 \text{ mg/cm}^2$ thereon, or a gel-forming coating thereon, the gel-forming coating

including a gel-forming polymer and a plasticizer.

Description of the Drawings

[0007] For the purpose of illustrating the invention, there is shown in the drawings a form which is present preferred; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities shown.

Figure 1 is a cross-sectional schematic illustration of a battery.

Figures 2-4 are graphical illustrations of the coatings' characteristics.

Detailed Description of the Invention

[0008] Referring to the drawings, wherein like numerals indicate like elements, there is shown in Figure 1 a battery 10. Battery 10 comprises a positive electrode 20, a negative electrode 30, and an electrolyte/separator system 40 therebetween. Electrolyte/separator system 40 comprises a microporous membrane 42, a gel electrolyte 44, and an adherent coating 46 therebetween.

[0009] In general, batteries 10 with negative and positive electrodes are well known and reference may be made to D. Linden (Ed.), Handbook of Batteries, 2d, McGraw-Hill Inc., New York, NY, (1995), U.S. Patent Nos. 5,296,318; 5,437,692; 5,460,904; 5,639,573; 5,681,357; and 5,688,293, and Japanese Patent Application Nos. 59-106556 (filed May 28, 1984), and 61-265840 (filed November 8, 1986) which are incorporated herein by reference. Preferably, the battery is a lithium ion battery, and most preferred is a lithium ion battery with a gel electrolyte.

[0010] Referring to electrolyte/separator system 40, its advantage is the inclusion of the adherent coating 46 between microporous membrane 42 and the electrolyte gel 44. The gel-forming polymer (and/or the combination of gel-forming polymer and electrolyte) has a tendency to delaminate or strip away from the microporous membrane 42. Accordingly, the adherent coating 46 is applied onto the surface of the microporous membrane 42 prior to application of the gel-forming polymer (and/or the combination of polymer and electrolyte) to facilitate bonding therebetween.

[0011] Microporous membrane 42 refers to any microporous membrane. Membrane 42 may be made from polyolefins. Exemplary polyolefins include, but are not limited to, polyethylene (PE), polypropylene (PP), and polymethylpentene (PMP). Membrane 42 may be made by either a dry stretch process (also known as the CEL-GARD process) or a solvent process (also known as the gel extrusion or phase separation process). Membrane 42 may have the following characteristics: an air permeability of no more than 300 sec/100cc (preferably 200

sec/100cc, most preferably 150 sec/100cc); a thickness ranging from 5 to 500 μ (preferably 10 to 100 μ , most preferably 10 to 50 μ); pore diameters ranging from 0.01 to 10 μ (preferably 0.05 to 5 μ , most preferably 0.05 to 0.5 μ); and a porosity ranging from 35 to 85% (preferably 40 to 80%). Membrane 42 is preferably a shut down separator, for example see U.S. Patent Nos. 4,650,730; 4,731,304; 5,281,491; 5,240,655; 5,565,281; 5,667,911; Application Serial No. 08/839,664 (filed April 15, 1997); Japanese Patent No. 2642206 and Japanese Patent Application Nos. 98395/1994 (filed May 12, 1994); 7/56320 (filed March 15, 1995); and U.K. Patent Application No. 9604055.5 (Feb. 27, 1996), which are incorporated herein by reference. Membranes 42 are commercially available from: CELGARD LLC, Charlotte, NC, USA; Asahi Chemical Industry Co., Ltd., Tokyo, Japan; Tonen Corporation, Tokyo, Japan; Ube Industries, Tokyo, Japan; and Nitto Denko K.K., Osaka, Japan.

[0012] Gel electrolyte 44 refers to a mixture of a gel-forming polymer and an electrolyte. During battery manufacture, the gel-forming polymer without the electrolyte may be applied to the microporous membrane 42, or the mixture of the gel-forming polymer and electrolyte may be applied to the membrane 42. Examples of the gel-forming polymer include, but are not limited to, polyvinylidene fluoride (PVDF); polyurethane; polyethyleneoxide; polyacrylonitrile; polymethylacrylate; polyacrylamide; polyvinylacetate; polyvinylpyrrolidone; polytetraethylene glycol diacrylate; copolymers of any of the foregoing, and combinations thereof. Electrolyte may be any electrolyte suitable for battery use.

[0013] The adherent coating 46 is applied to a surface of membrane 42, preferably both the exterior surface and pore interior surfaces, and is interposed between membrane 42 and gel electrolyte 44 (or gel-forming polymer), and does not adversely affect ion conductivity (e.g., by pore blockage), and does not materially increase membrane thickness or decrease membrane flexibility, and increases adhesion between or decreases delamination of the membrane 42 and gel electrolyte 44 (or gel-forming polymer). In this aspect of the invention, the coating 46 is used in addition to gel-forming polymer layer (or gel electrolyte) and is not a substitute therefor.

[0014] Coating 46 may be applied to membrane 42 in the form of a dilute solution of an active ingredient and a solvent. Coating 46, to achieve suitable adhesion, should have a surface density in the range of less than 0.3 mg/cm² (preferably in the range of 0.05 to less than 0.3 mg/cm²; and most preferably 0.1 to 0.25 mg/cm²). The active ingredient is chosen, in one aspect, so that the surface energy of the coating (γ_c) is equal to or less than the surface energy of the membrane (γ_m). For example, typical membranes materials include polyethylene (γ_{PE} : about 35-36) and polypropylene (γ_{PP} about 29-30). See, for example, A.F.M. Barton, Handbook of Solubility Parameters, 2d., C.R.C. Press, (1991), P. 586.

Exemplary active ingredients include, but are not limited to, polyvinylidene fluoride (PVDF), polyacrylates, and polyacronitriles, copolymers thereof (e.g., PVDF copolymers, and more specifically PVDF:HFP (HFP : hexafluoropropylene or hexafluoropropene) copolymer) and mixtures thereof. The γ_{PVDF} is about 32, and $\gamma_{PVDF:HFP} \leq 25$. The solvent is chosen so that it can dissolve the active ingredient. Exemplary solvents include, but are not limited to, organic solvents, e.g., tetrahydrofuran, methyl ethyl ketone (MEK), and acetone. The dilute solution may contain less than 10% by weight of the active ingredient. Figure 2-4 illustrate surface density (mg/cm²), MacMullin Number (e.g., see U.S. Patent No. 4,464,238), and adhesion (pounds/inch) as a function of % PVDF: HFP copolymer in solution (tetrahydrofuran). The notation 'xDBP' refers to equivalent amounts of plasticizer (DBP) to active ingredient.

[0015] The process to make a battery with a separator having the adherent coating may comprise the following steps: coating a microporous membrane with the mixture of active ingredient and solvent, and thereafter drying the separator; coating the separator with the gel-forming polymer; laminating the anode, coated separator, and cathode, to form a battery without electrolyte; placing that battery into a 'bag' (e.g., the leak-tight, flexible package that replaces the 'can'); adding electrolyte to the bag; and curing the battery to form the gel electrolyte, whereby the active battery is formed.

[0016] In an alternate embodiment, the absorbing or gel-forming layer discussed in U.S. Patent Nos. 5,639,573; 5,681,357; and 5,688,293, incorporated herein by reference, is improved by the inclusion of a plasticizer. The plasticizer's primary function is to act as an extractable filler in the densely-coated (i.e., ≥ 0.3 mg/cm²), absorbing or gel-forming layer. The plasticizer is necessary in the densely-coated layer because of the layer's tendency to blind pores or reduce the pore's diameter in the microporous membrane, and consequently reduce conductivity. Exemplary plasticizers include, but are not limited to, esters, e.g., phthalate-based ester, such as dibutyl phthalate.

[0017] The process to make a battery with a separator having a coating of a gel-forming polymer and a plasticizer may comprise the following steps: coating a microporous membrane with a solvated mixture of polymer and plasticizer; thereafter drying the separator; laminating (e.g., under heat and pressure) the anode, separator, and the cathode to form a battery without electrolyte; removing the plasticizer (e.g., by extraction with a suitable solvent, e.g., methanol); placing that battery into a 'bag'; and adding electrolyte to the bag, whereby the active battery is formed.

[0018] The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

Claims

1. A battery separator comprising:

a microporous membrane; and 5
 an adherent coating thereon, said coating hav-
 ing a surface density $< 0.3 \text{ mg/cm}^2$
2. The separator of claim 1 wherein said surface den-
 sity ranges from 0.05 to $< 0.3 \text{ mg/cm}^2$. 10
3. The separator of claim 1 wherein said surface den-
 sity ranges from 0.1 to 0.25 mg/cm^2 .
4. The separator of claim 1 wherein said adherent 15
 coating comprises an active ingredient selected
 from the group consisting of polyvinylidene fluoride,
 polyacrylates, polyacronitriles, copolymers thereof
 and mixtures thereof. 20
5. The separator of claim 4 wherein said active ingre-
 dient is a poly(vinylidene fluoride;hexafluoropropyl-
 ene) copolymer.
6. A battery with the separator of claim 1. 25
7. The battery of claim 6 being a lithium ion battery.
8. A battery separator comprising: 30

a microporous membrane, said membrane
 having a surface energy (γ_m) ; and

 an adherent coating thereon, said coating hav-
 ing a surface energy (γ_c) ; wherein $\gamma_c \leq \gamma_m$. 35
9. A battery separator comprising:

a microporous membrane; and
 a gel-forming coating thereon, said coating 40
 comprising an absorbing or gel-forming poly-
 mer and a plasticizer.
10. The battery separator according to claim 9 wherein
 said plasticizer is an ester. 45
11. The battery separator according to claim 10
 wherein said ester is a phthalate.
12. The battery separator according to claim 11 50
 wherein said phthalate is dibutyl phthalate.
13. A battery with the separator of claim 9.
14. The battery of claim 13 being a lithium ion battery. 55

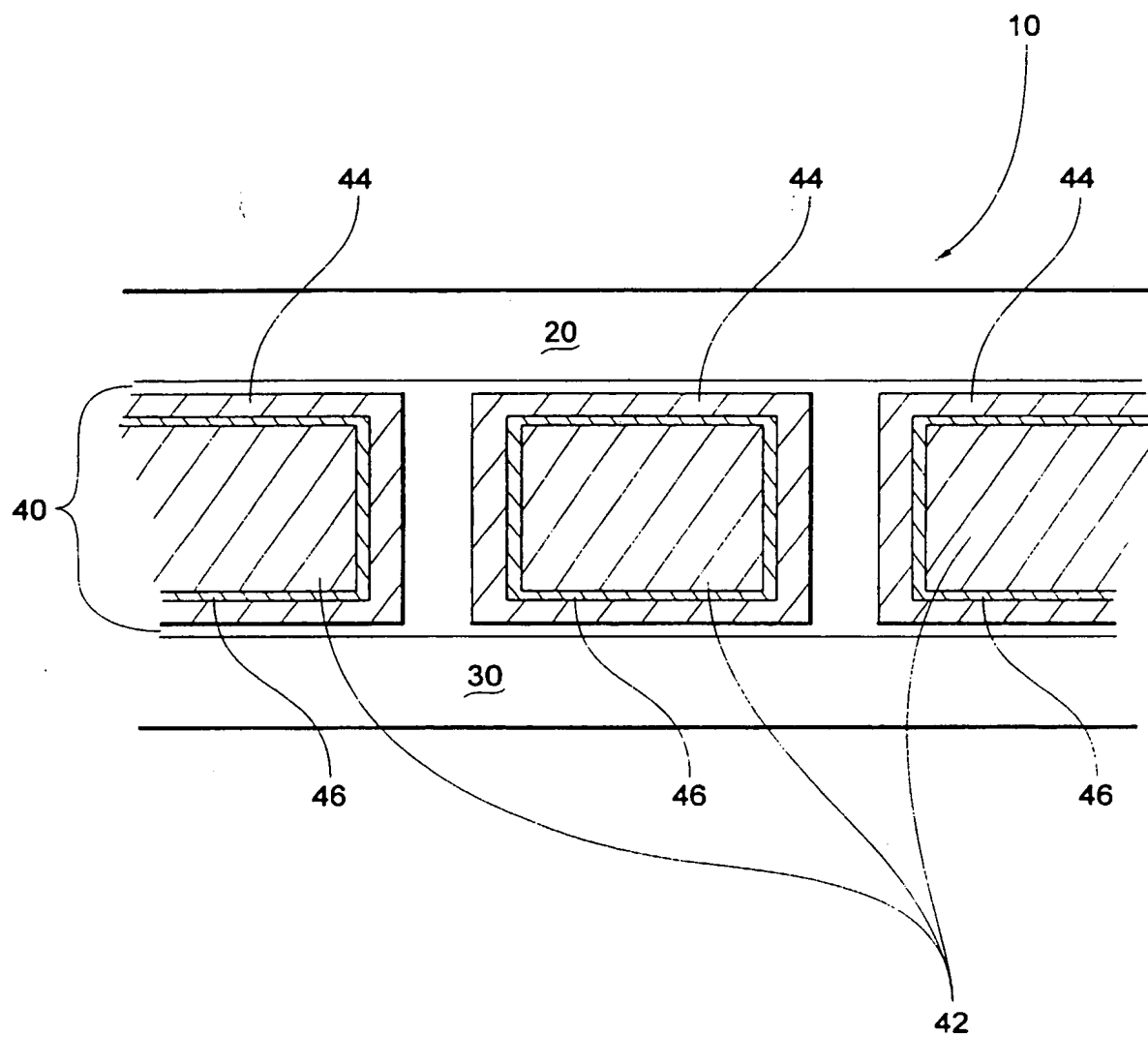


Fig. 1

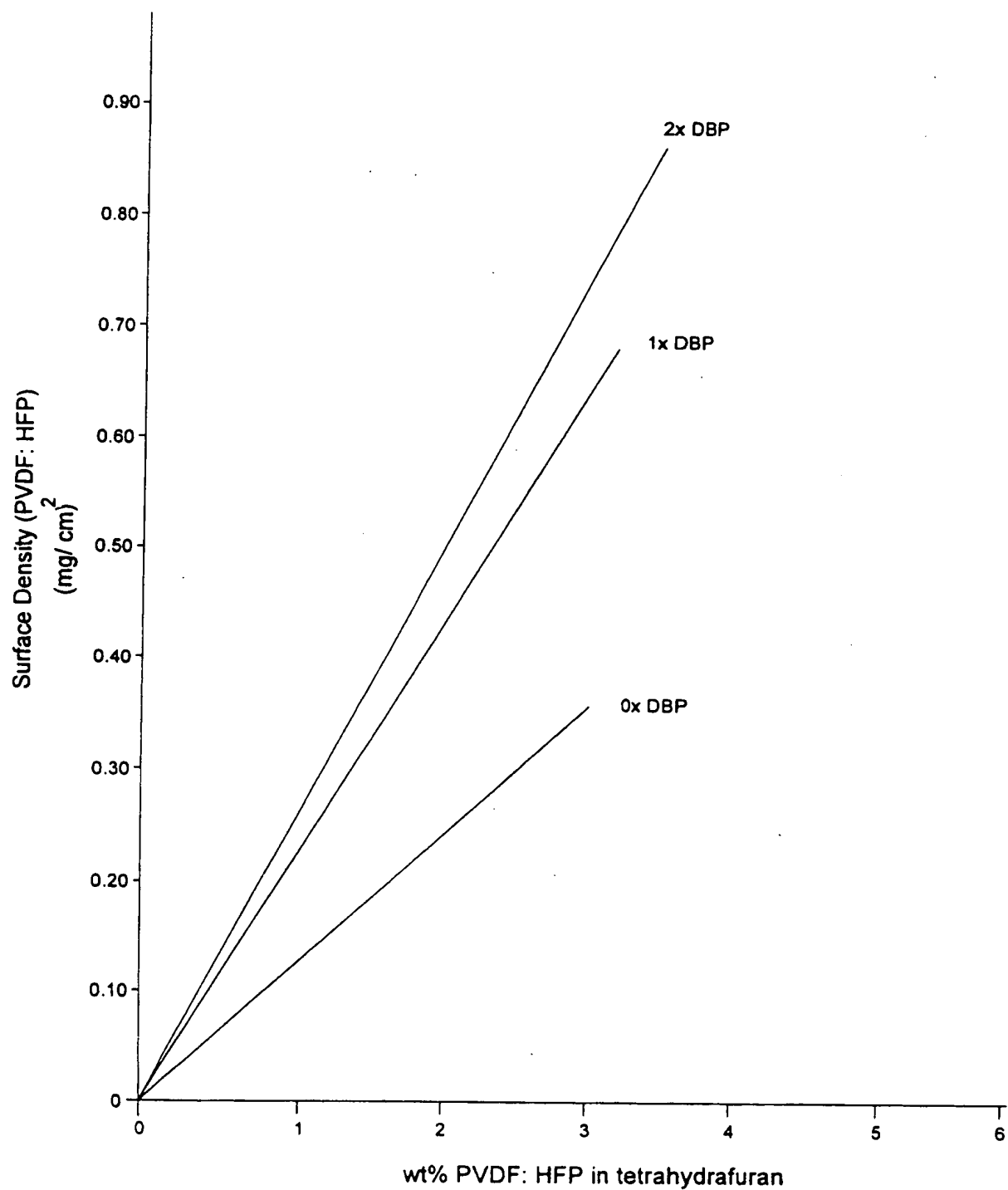


Fig. 2

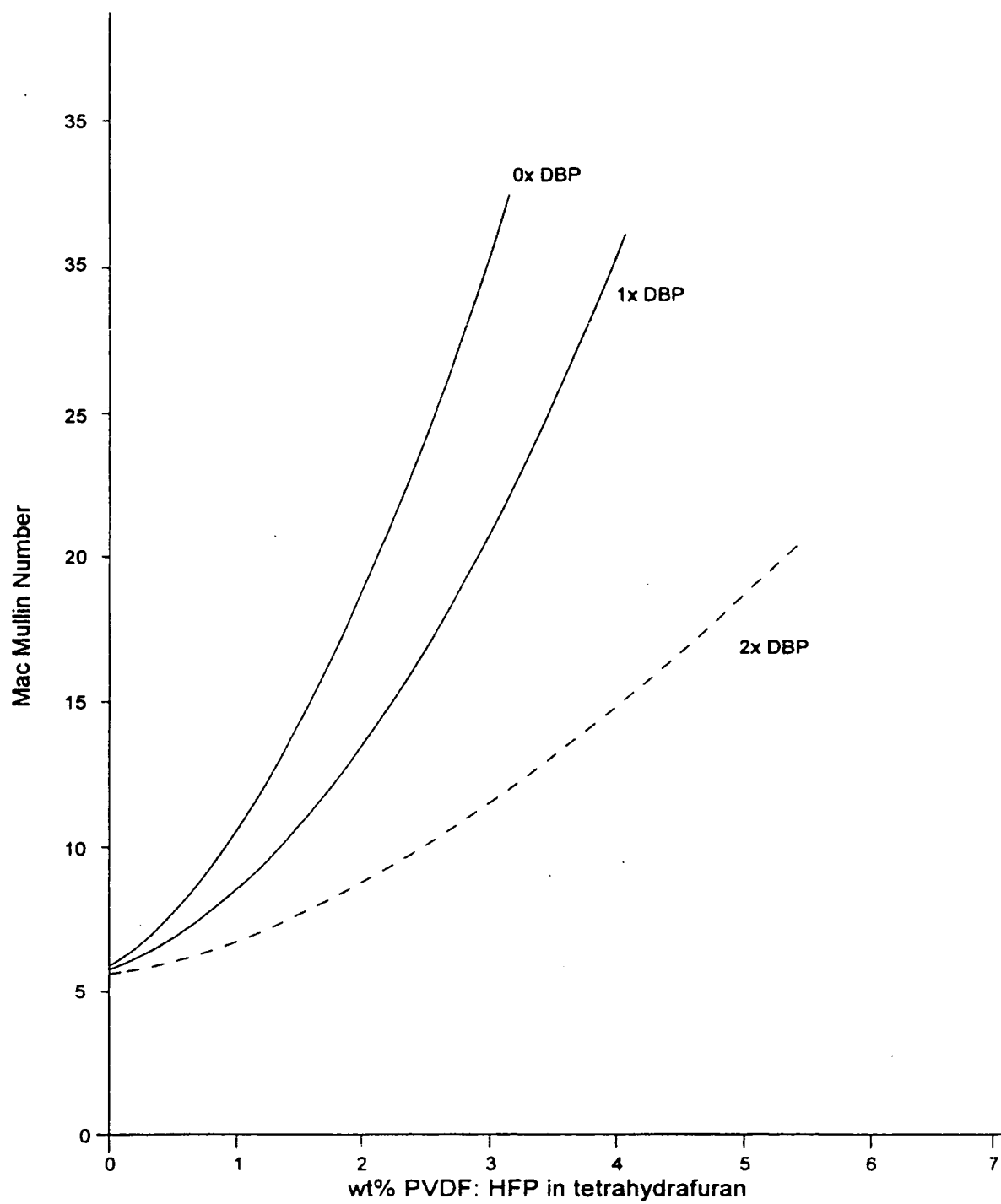


Fig. 3

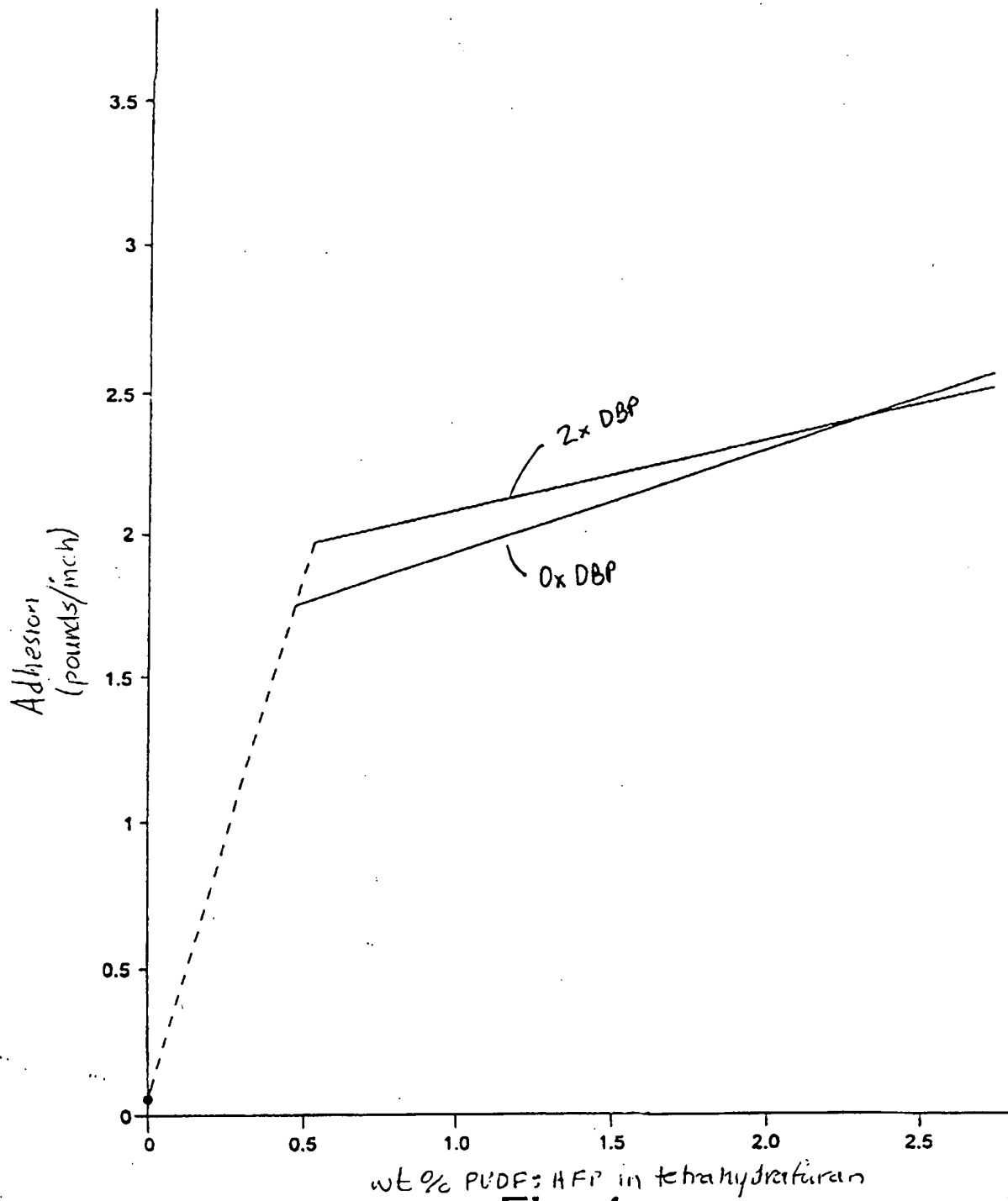
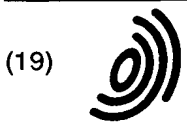


Fig. 4



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 933 824 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
26.07.2000 Bulletin 2000/30

(51) Int. Cl.⁷: **H01M 2/16**, **H01M 10/40**

(43) Date of publication A2:
04.08.1999 Bulletin 1999/31

(21) Application number: **99101376.4**

(22) Date of filing: **26.01.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• **Spotnitz, Robert M.**
San Remo, CA 94538 (US)
• **Wensley, Glen C.**
Rock Hill S.C. 29732 (US)

(30) Priority: **30.01.1998 US 16024**

(71) Applicant: **Celgard Inc.**
Burlington, Massachusetts 0183 (US)

(74) Representative:
von Kreisler, Alek, Dipl.-Chem. et al
Patentanwälte,
von Kreisler-Selting-Werner,
Bahnhofsvorplatz 1 (Deichmannhaus)
50667 Köln (DE)

(54) **Separator for gel electrolyte battery**

(57) A battery separator (40) for a gel electrolyte
(44) battery (10) includes a microporous membrane
(42); and an adherent coating (46) thereon, or a gel-

forming coating thereon, the gel-forming coating includ-
ing a gel-forming polymer and a plasticizer.

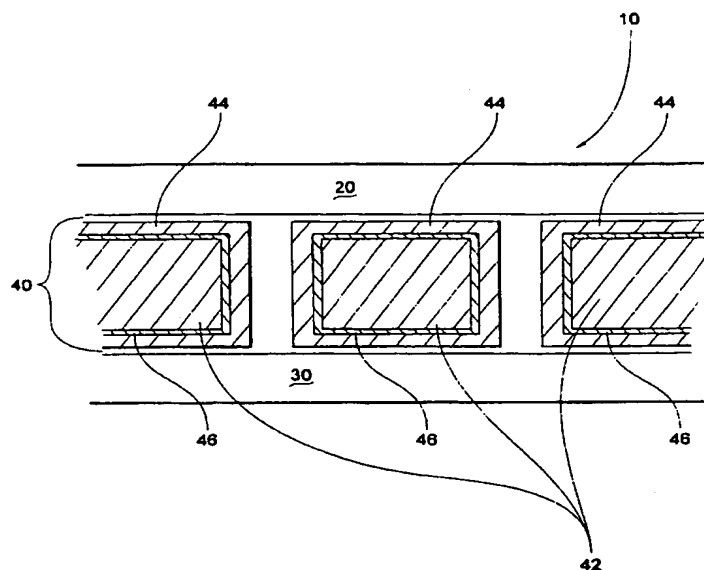


Fig. 1

EP 0 933 824 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 10 1376

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	US 5 639 573 A (OLIVER MANUEL ET AL) 17 June 1997 (1997-06-17) * column 3, line 44 - column 4, line 30; figure 2 *	1-8	H01M2/16 H01M10/40
D,X	US 5 681 357 A (ESCHBACH FLORENCE O ET AL) 28 October 1997 (1997-10-28) * column 4, line 21 - line 65 *	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01M
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		16 December 1999	GREGG, N
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04C01)



European Patent
Office

Application Number
EP 99 10 1376

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-8



European Patent
Office

**LACK OF UNITY OF INVENTION
SHEET B**

Application Number
EP 99 10 1376

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-8

A battery separator comprising a microporous membrane having a coating thereon which promotes adhesion with the electrolyte

2. Claims: 9-14

A battery separator comprising a microporous membrane and a coating comprising a gel-forming polymer and a plasticizer

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 10 1376

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-12-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5639573 A	17-06-1997	US 5658685 A	19-08-1997
		CN 1216164 A	05-05-1999
		EP 0846346 A	10-06-1998
		WO 9708765 A	06-03-1997
-----	-----	-----	-----
US 5681357 A	28-10-1997	WO 9812766 A	26-03-1998
-----	-----	-----	-----

THIS PAGE BLANK (USPTO)